Molybdenum induced inhibition of Titania films and ethanol sensing properties

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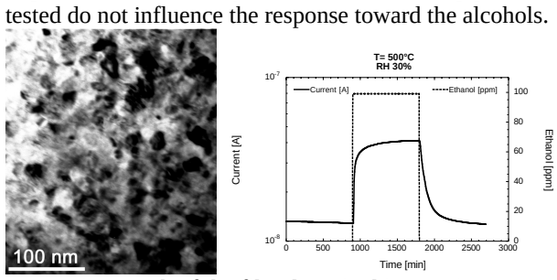
During the last years the demand of systems for gas analysis was increasing. The necessity of materials with good sensing properties has to be correlated with a deeper understanding of structural and electrical properties of the thin films used as sensing elements. It is important to prepare thin films with high sensitivity toward the gas environment and long term stability at the operation temperatures. Sensitivity is related to both surface reactivity and to the surface exposed for gas adsorption [1]. The reactivity of the surface of a semiconductor-oxide thin film is a property strictly related to the completion of oxygen in the lattice: as the oxide becomes more stoichiometric the reactivity of the surface decreases, though the film becomes more stable for long-term operation. Nanostructured materials have a large specific area and therefore are good for gas sensing. Thermal treatment yields stability to the film for long-term operation, but affects negatively the surface reactivity and the specific surface, leading to oxidation of the film and grain coalescence. A compromise between performance and stability has to be reached, but this often results in a difficulty to achieve good sensing materials. It was found out a threshold in grain size for sensing at moderate temperature: as the average size of the grains exceeded 80-100 nm, the sensitivity fell off severely [2]. Many investigations has been made on the way to prevent grain growth in titania films mantaining high sensitivity; it has been found out that the addition of a suitable element may inhibit coalescence versus annealing. Dopants such as Nb or Ta proved useful for such a purpose [2]. It was also found that a Fe_2O_3 phase co-deposited with titania, segregated at the boundaries between grains and prevented further growth [3]. A big effort is to be put in modifying the reactivity of the surface of titania grains without appreciably affecting grain growth.

In this work, we have deposited titania films via RF sputtering of a Ti/Mo mixed metallic target. Molybdenum was chosen because it is chemically very similar to tungsten, whose inhibition properties to exaggerated grain growth in titania have been extensively studied in the past [4]. In order to achieve films with diverse reactivity, we deposited films in inert or reactive atmosphere and comparatively discussed both structural and electrical features. Depositions were executed by using magnetron sputtering by a metallic target of Ti and Mo with a weight percentage of 98.6% and 1.4%, respectively. Two different kinds of atmospheres were used: an inert atmosphere of pure Ar and a reactive atmosphere of Ar and O_2 with a total pressure of 8×10^{-3} mbar. Part of the thin films were studied just after deposition while the others underwent two different oxidation cycles.

The structural evolution of the Ti-Mo-O layers, resulted from electron microscopy analysis, can be summarized as follows. The film deposited in inert atmosphere featured nucleation of TiO_2 rutile from the amorphous Ti-based matrix after annealing at 600°C. The number of rutile nucleation sites in the amorphous matrix resulted to be limited and grain growth followed at fast rate, resulting in a relatively large grain size for the oxidized part of the layer. Evidence for incomplete oxidation for the film together with the absence of TiO_2 anatase phase indicates that a relatively high activation energy was required for nucleation of the oxide. As far as the layers deposited in reactive atmosphere are concerned, their small particle size resulted from a different growth mechanism. In fact, the nucleation of TiO_2 in the as-deposited film limited the increase of particle dimension upon annealing as competition between particles occurred during sintering. Formation of TiO_2 rutile also promoted diffusion of Mo towards the surface, where oxidation and sublimation occurred. The characterization showed that achievement of TiO_2 starting from a Ti-Mo-O layer resulted in a relatively fine-grained polycrystalline film even after annealing at 800°C. Pure titania is indeed known to suffer exaggerated coalescence when annealed at such an high temperature. The presence of Mo inhibited the grain growth of titania, thereby resulting in a nanosized TiO_2 structure. Both methods took advantage of addition of a part of Mo, which proved useful to prevent exaggerated coalescence of nanograins.

We have investigated the sensing capability of the layers toward ethanol as a target gas. The response vary as the degree of oxidation of layer increases and also the stability of the electrical properties are strictly correlated. The response and recovery times for ethanol are particularly interesting for thinking possible applications like control food analyses, wine identifications, electronic noses and medical devices. The response is very high at concentration below the limit imposed for breath analysers and the interfering gases tested do not influence the response toward the alcohols.



TEM micrograph of the film deposited in reactive atmosphere and response toward 100 ppm of Ethanol for the layer deposited in a reactive atmosphere.

Reference:

1 N. Yamazoe and N. Miura, in Some basic aspects of semiconductor gas sensors in Chemical Sensor Technology, Eds. S. Yamauchi, Kodansha (Elsevier, Amsterdam, 1992) vol. 4, p. 19
2 V. Guidi, M.C. Carotta, M. Ferroni, G. Martinelli, L. Paglialonga, P. Nelli, G. Sberveglieri Sensors and Actuators B 57 (1999) 197
3 E. Comini, V. Guidi, C. Frigeri, M. Ferroni, D. Boscarino, G. Sberveglieri in press in Journal of Material Research
4 M. Ferroni, V. Guidi, G. Martinelli, E. Comini, G. Sberveglieri, D. Boscarino, G. Della Mea, Journal of Applied Physics 88 (2000) 1097